

Attachment IX.

Esters as Lubricating Oils.

Esters as Lubricant Improvers.

I. G. Leuna Report by Dr. H. Zorn

Report presented at the
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I shall give you briefly an insight into the significance of the addition of esters to lubricating oils.

One of the most important properties of a lubricant is its viscosity-temperature behavior. This may be specified by viscosity index, the so-called VI. value according to the American proposal. The higher the VI. value, the lower is the dependence of viscosity on temperature and therefore the flatter is the viscosity-temperature curve. Another method of characterization employs a logarithmic plot of absolute temperature and viscosity according to a proposal of Walther and Ubbelohde (cf. Figure 1). The viscosity-temperature curve then becomes a straight line. The slope of this straight line as expressed by the m-value, is then an index for the viscosity-temperature behavior of the lubricant. Walther and Ubbelohde make the further assumption that the curves (i.e., straight lines) for oils of different viscosity but from the same source intersect at one point, the "viscosity pole". The smaller the distance of this viscosity pole from the abscissa, i.e., the smaller the "viscosity pole height", the lesser is the dependence of viscosity on temperature. For the latter, small m- and VI values are required.

The dependence of the viscosity-temperature behavior of esters on their chemical constitution is shown in the following figures. X

Table 2 shows esters formed from tri- and tetra-hydroxy alcohols esterified with various acids. First let us compare the esters of normal octylic acid. It appears that there is no difference between trimethylolethane and trimethylolpropane in regard to magnitude of viscosity and viscosity-temperature behavior but there is considerable difference in low-temperature behavior (i.e., pour point), the ester of trimethylolpropane being superior to that of trimethylolethane by 61°. Glycerol is equivalent to both alcohols in regard to viscosity-temperature behavior; however, the magnitude of viscosity is smaller and the pour point appreciably higher than for trimethylolpropane but lower than for trimethylolethane. Pentaerythritol gives an ester of appreciably higher viscosity, still higher pour point, and somewhat better viscosity-temperature behavior. It is very interesting to compare the esters of the four alcohols with a branched-chain acid, namely, 2-ethylhexanoic acid. The pour points of these four esters are all very low. There is no difference here between trimethylolethane and trimethylolpropane. The ester of glycerol has the lowest viscosity, that of pentaerythritol again the highest viscosity and similarly the best viscosity-temperature behavior. If, instead of 2-ethylhexanoic acid, the mixture of carboxylic acids is taken which is formed by the alcohol fraction from isobutyl alcohol boiling at 200°-250°, then esters are obtained which are equivalent to those mentioned above in regard to viscosity behavior, but not so favorable in regard to pour point. The pour point of the glycerol esters is remarkable. Esters of this type can be used in the coatings industry as softeners and in the electrical industry as switch oils. It is very interesting to observe the effect of incomplete esterification of these alcohols on viscosity-temperature behavior. These relationships are shown in Table 3.

It is evident that, for trimethylolethane as well as pentaerythritol, the viscosity becomes higher and the viscosity-temperature relation becomes poorer, the more free hydroxyl groups are present in the esters. This is altogether understandable, for free hydroxyl groups cause a strong association of the ester molecules. All the alcohols are well known to be strongly associated. It is interesting that this association, i.e., formation of molecular complexes, proceeds altogether uniformly as shown in experiments conducted at Halle by Prof. Wolff and co-workers at my suggestion. Equal numbers of 1, 2, 3, 4, and up to 12-fold molecules are present in the whole mass.

The investigation of esters of dihydroxy glycols is reviewed in Table 4. Ethylene glycol, tetramethylene glycol, hexamethylene glycol, methylhexamethylene glycol, and dimethylolpropane were investigated. It appears that, in the case of the esters of straight-chain glycols with normal octanoic acid, there is an increase in viscosity and a decrease of the m -value (i.e., improvement in viscosity-temperature behavior) with increasing molecular weight. It is interesting that the pour point is lowered with methylhexamethylene glycol and dimethylolpropane. The influence of the methyl group is again noticeable here as was seen in the case of the hydrocarbon, hexadecane. The pour point is very favorably affected when isoöctanoic acid or Leuna carboxylic acid is employed instead of normal octanoic acid. However, the viscosity-temperature behavior is somewhat less favorable with these branched-chain acids.

A study of the esters of adipic and methyladipic acids is presented in Table 5. It is interesting to compare the esters of normal octanol and isoöctanol. The latter has outstanding low-temperature behavior (pour point) because of the influence of the ethyl side chain. The effect of the methyl group is seen to be quite analogous on comparing cyclohexanol with methylcyclohexanol. Both these esters show higher viscosity and a less favorable viscosity-temperature behavior than do the octanol esters. The esters of methyladipic acid are only insignificantly different from corresponding ones of adipic acid in regard to viscosity-temperature behavior, but are partially more favorable to an appreciable extent in regard to low-temperature behavior. Especially interesting from a practical viewpoint is the cyclohexanol ester of β -methyladipic acid. This finds application as a watch or clock oil, for it does not spread on a metal surface but stays together in drops. Furthermore, it has an outlet as an additive in our aircraft hydraulic oil.

The influence of the methyl group in dicarboxylic acids is exhaustively treated in Table 6. Let us compare the normal octanol and normal dodecanol esters of α - and β -methyladipic acid with those of adipic acid. It is striking here that the esters of α -methyladipic acid are consistently somewhat less favorable in regard to viscosity-temperature behavior than those of β -methyladipic acid. This is a striking example of the importance of the position of the side chain in the molecule. If the acids are esterified with branched-chain alcohols as, for example, our Leuna alcohols or alcohols which are obtained by applying the "Oxo" process to diisobutylene, esters are obtained of very outstanding low-temperature behavior. The esters of sebacic acid are especially noteworthy for they combine good pour point with outstanding viscosity-temperature behavior and consequently excel the esters of adipic acid. The ester of β -methyladipic acid with Leuna alcohols finds

+ Treatment with CO and H₂.

an outlet in the preparation of motor oils suitable for low-temperature operation and axle oils; some were also found suitable as softeners for Igelite (resin or plastic?).

The effect of increase in molecular size on viscosity-temperature behavior is shown in Table 7. The polyhydroxy alcohols were esterified both with normal octanoic acid and with long-chain semi-esters of adipic acid and Leuna alcohol fraction boiling from 140° to 180° (i.e., largely C6 and C7 alcohols). It appears that the latter esters are appreciably more viscous and somewhat more favorable in regard to viscosity-temperature behavior than are the esters of normal octanoic acid. It is quite understandable that the low-temperature behavior of this ester as shown by pour point should be outstanding, since the branched-chain Leuna alcohol is incorporated in the semi-ester. Furthermore, the lubricating qualities of esters of this type are very good. They have found a practical application as cutting oils. It is also possible to lengthen the straight chain of the molecule by ethoxylating an alcohol.

Results of the investigation of this subject are given in Table 8. First, the iso-C9-alcohol mixture obtained by the "Oxo" process on diisobutylene was employed as the alcohol. It is evident from Table 8 that the viscosity rises and the viscosity-temperature behavior improves with increasing ethylene oxide content. On the other hand, the low-temperature behavior becomes poorer the more ethylene oxide is taken up. It is very interesting to compare the products from Leuna alcohol which have been treated with two moles of ethylene oxide and esterified with adipic, methyladipic, and sebacic acids. The low-temperature behavior of these three esters is exactly similar; the viscosity rises and the viscosity-temperature behavior improves in the order adipic, methyladipic, and sebacic acid. Here, too, the sebacic acid ester is the most favorable. Unfortunately, these esters have the disadvantage that they are poorly miscible with hydrocarbon oils or even completely immiscible when they contain much ethylene oxide. More than one molecule of ethylene oxide must not be taken up; with two moles of oxide miscibility with hydrocarbon oils is already lost at room temperature. However, this ester is completely miscible at higher temperatures (e.g., 80°). With still higher molar proportions of oxide, even the miscibility at higher temperatures is lost.

After we had studied the relation between the constitution of esters and their viscosity characteristics to some extent, we proceeded to investigate the relation between their constitution and lubricating properties. The results of this investigation are shown in Figure 9. Curves 1, 2, and 3 of Figure 9 are values for adipic acid esters of the straight-chain alcohols, butanol, octanol, and dodecanol. It is evident that the coefficient of friction falls and the dependence of coefficient of friction on temperature steadily improves with increasing molecular weight. If the adipic acid in these esters is replaced by methyladipic acid (so as to give Esters 4 and 5), it is evident that the coefficient of friction for the methyladipic acid esters is always higher than for the corresponding adipic acid ester. This influence of the methyl group is again confirmed on comparing Esters 2 and 6 as well as 6 and 7 (cf. Figure 10). The right-hand plot is interesting, which shows wear values measured by a hard metal disc pressed against a steel plate. It is evident here that the ester which gives the highest coefficient of friction also gives the lowest wear value.

Figure 11 again shows a sharp decrease in coefficient of friction with increasing molecular weight of the ester (compare No. 25 with 11, 12, 13 and 16). The temperature dependence becomes steadily more favorable. In the case of Ester 16, a small decrease in coefficient of friction with increasing temperature was observed. Furthermore, it is interesting to compare 11 and 12: The branched-chain acid again shows the higher coefficient of friction and the stronger dependence of coefficient of friction on temperature. It is also interesting that the coefficient of friction is only slightly increased by incomplete esterification and the temperature dependence is not affected at all (cf. 17 and 13). In the wear experiments, the order of rating of the esters is again just the reverse as for coefficient of friction. Also in the case of the still higher molecular esters, it is confirmed that the coefficient of friction decreases and the μ -temperature curve becomes flatter with increasing molecular weight as shown in Figure 12. This interesting reversal in behavior between lubricating quality, as characterized by coefficient of friction, and wear arises from the force with which molecules are held on the surface. The work which must be expended in tearing loose a 1-sq. cm. cross section of the liquid from the interface is defined as energy of adhesion. It can be determined by measuring the interfacial tension γ and surface tension σ of both phases. The Dupr e rule holds here: $H = \sigma_1 + \sigma_2 - \gamma_{12}$. Prof. Wolff at Halle investigated numerous materials with reference to their energies of adhesion at my suggestion. Some results of this investigation are shown in Table 13.

With reference to hydrocarbons, it is interesting to note the behavior of benzene, which is held appreciably more firmly on mercury than is its hydrogenation product, cyclohexane. In the series of alcohols, an increase in energy of adhesion is observed with increasing length of the carbon chain. It is noteworthy that branching of the carbon chain causes a diminution in energy of adhesion. In the case of acids, the energy of adhesion is altogether independent of molecular size. This results from the fact that the dimeric molecular association occurs with all acids. Greater than two-fold molecular complex formation occurs only in the case of formic acid. With esters, just as in the case of alcohols, we observed an increase in the energy of adhesion with increasing molecular weight of the alcohol constituent. It is noteworthy here that branching of the alcoholic carbon chain does not entail an increase in the energy of adhesion. The reason for this different behavior as compared with the straight alcohols probably lies in the manner in which the molecules are oriented at the interface. There are two possibilities here - either they stand upright with their carbon chains perpendicular to the interface, or they lie down tangentially. The question as to which orientation is favored for a given type of material depends both on the steric location of the dipole group in the molecule and on the position and magnitude of the permanent dipole within the group. The energies of adhesion are naturally dependent not only on the lubricant but also on the other phase in contact with it. The differences between energies of adhesion for various materials against an aqueous and against a metallic surface are collected in Table 14. It is evident that there is a large difference between water and mercury. The several materials adhere to mercury on the average two to three times as strongly as to water. The adhesive resistance can be calculated from the energy of adhesion.

Table 15 gives the corresponding values for hydrocarbons, alcohols, and acids. It is again evident that the adhesive resistance increases with increase in degree of unsaturation for hydrocarbons, with increase in carbon chain length for alcohols, and is independent of the molecular size for acids. These adhesive resistances, which are a measure of the force required to tear away a surface of 1 sq. cm. cross section, correspond to the internal resistance to rupture within the liquid or the metal. The latter is calculated from the interfacial tension; it denotes the resistance to rupture. The magnitude of these values for liquids is remarkable. The rupture of a liquid organic acid requires the same force or perhaps even greater force than does the rupture of a metal such as brass or iron. Without further ado, this fact explains the reversal of behavior between coefficient of friction and wear. The greater the adhesive resistance of a lubricant, the stronger is the lubricating film and therefore the smaller is the coefficient of friction but, on the other hand, the larger is the force with which a liquid molecule can tear a metal atom out of its surface. Consequently, when we wish to obtain low wear, we should not develop lubricants which show extraordinarily high adhesive resistance, but rather we should only approach an optimum. In order to arrive at this goal, we must direct our attention not so much at the dipole forces of the molecule, but rather at the dispersion forces of the molecule which arise from the specific quantum binding of the carbon chain.

However, not only the lubricant but also the other phase (namely the metal) is responsible for wear. Figure 16 shows the different wear behavior of various metals against the same lubricant. A material (e.g., polyether alcohol LK-2200) can have extraordinarily strong antiwear properties against red brass but causes wear of soft metals to such an extent that one can almost say that the metal is dissolved by the liquid. Also a straight mineral oil (e.g., Oil K7) behaves very differently against various metals.

This difference in behavior of oils against various metals is naturally reflected in actual lubrication. If consideration is given to the various states of lubrication of the journal bearing in Figure 17, the chemical constitution of the lubricant becomes important in the range where the speed of rotation is low and the loading correspondingly high. This is the region of partial lubrication (quasi-hydrodynamic) and boundary lubrication.

The difference in behavior of various bearing metals against the same oil in a state of boundary lubrication is shown in Figures 18, 19, and 20. These experiments were carried out by Prof. Heidebroeck at Dresden. It is evident that the transition point from hydrodynamic to boundary lubrication at the same degree of loading varies with the nature of the bearing metal and the oil. It is a question here of the action of the boundary surface forces in thick films of liquid. That orientation must extend from the boundary surface into fairly deep layers of the liquid appears still more probable on comparing the action of two different bearings with the same oil (cf. Figure 21). It is evident that, with a given bearing clearance, different oil pressures must be employed for passage of a definite quantity of oil per unit time, depending on the nature of the bearing material.

FIGURE 1 - VISCOSITY-TEMPERATURE LINES FOR TWO SERIES OF OILS

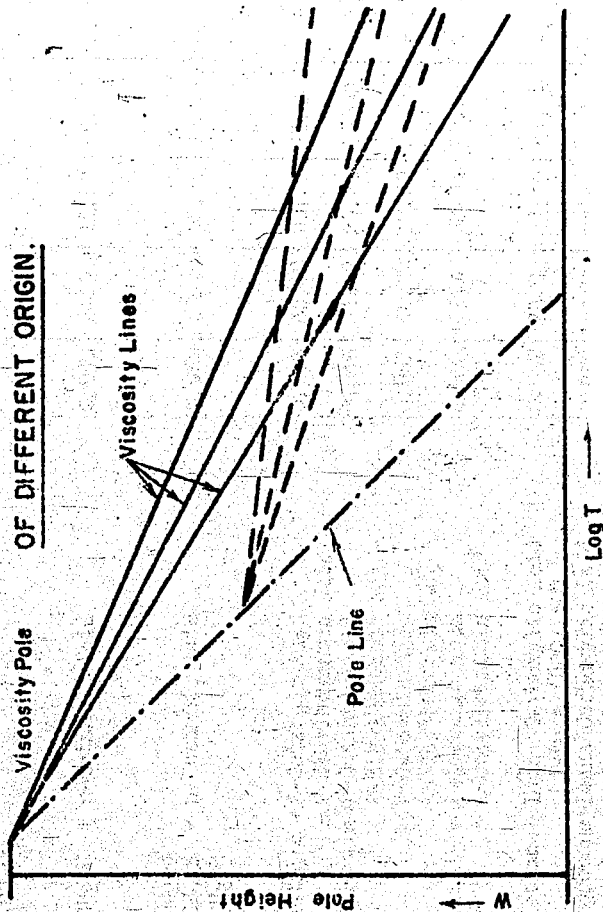


Table 2

Esters of Tri- and Tetra-Hydroxy Alcohols	Spec. Gr. 20°C	Viscosity in cs., °C				m 20:99	Pour Point °C
		20	38	50	99		
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + \text{n-Octanoic Acid}$	0.944	36.20	17.75	11.95	3.86	3.58	-8
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2\text{OH} \\ \quad \backslash \\ \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \end{array} + \text{n-Octanoic Acid}$	0.948	37.00	18.00	12.20	3.96	3.57	-69
$\begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}-\text{CH}_2\text{OH} \\ \\ \text{OH} \end{array} + \text{n-Octanoic Acid}$	0.940	25.34	12.97	8.98	3.20	3.57	-24
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{HO}-\text{CH}_2-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} + \text{n-Octanoic Acid}$	0.959	50.79	23.80	15.69	4.73	3.50	+7
Trimethylolmethane + 2-Octanoic Acid	0.948	49.30	20.90	13.5	3.84	3.88	-63
2-Ethylhexanoic Acid							
Trimethylolpropane + 2-Octanoic Acid	0.948	64.92	26.28	16.09	4.17	4.02	-58
2-Ethylhexanoic Acid							
Glycerol + 2-Octanoic Acid	0.952	40.27	17.39	11.10	3.21	4.11	-66
2-Ethylhexanoic Acid							
Pentaerythritol + 2-Octanoic Acid	0.965	143.7	52.01	29.94	6.37	3.91	-45
2-Ethylhexanoic Acid							
Trimethylolmethane + Leuna Carboxylic Acid mixture (200/250)	0.949	123.0	42.50	24.75	5.57	3.96	-48
Trimethylolpropane + Leuna Carboxylic Acid mixture (200/250)	0.958	144.7	50.20	28.60	6.30	3.97	-49
Glycerol + Leuna Carboxylic Acid mixture (200/250)	0.954	94.4	34.0	20.7	4.93	3.96	-60
Pentaerythritol + Leuna Carboxylic Acid mixture (200/250)	0.961	453.0	117.2	63.5	10.45	3.88	-31

Table 3

Esters of Tri- and Tetra-Hydroxy Alcohols Incomplete Esterification	Spec. Gr. 20°C	Viscosity in cs., °C				m 20:99	Pour Point, °C
		30	38	50	99		
Trimethylolmethane + 3 Moles i-C ₁₃ Acid	0.917	97.90	42.13	26.66	7.11	3.54	-28
Trimethylolmethane 2 Moles i-C ₁₃ Acid	0.925	124.5	49.90	29.87	7.27	3.51	-27
Trimethylolmethane 3 Moles Leuna Carboxylic Acid	0.949	125	42.50	24.8	5.57	3.96	-48
Trimethylolmethane 2 Moles Leuna Carboxylic Acid	0.962	193	59.50	32.40	6.57	4.01	-44
Trimethylolmethane 1 Mole Leuna Carboxylic Acid	0.982	427	105	51.5	7.80	4.34	-53
Pentaerythritol 4 Moles i-C ₁₃ Acid	0.929	279.50	71.10	42.80	10.00	3.27	-28
Pentaerythritol 3 Moles i-C ₁₃ Acid	0.934	213.2	81.20	48.50	10.40	3.33	-27
Pentaerythritol 2 Moles i-C ₁₃ Acid	0.951	339.0	114.9	64.50	11.70	3.50	-26

Table 4

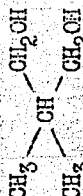
Esters of Dihydroxy Glycols	Spec. Grav. 20°C	Viscosity in cs., °C				m 20:99	Pour Point, °C
		20	38	50	99		
HO-CH ₂ -CH ₂ -OH + n-Octanoic Acid	0.934	9.00	5.36	4.03	1.76	3.67	+18
HO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH + n-Octanoic Acid	0.919	11.77	6.85	5.17	2.29	3.38	+13
HO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH + n-Octanoic Acid	0.930	14.40	8.40	6.25	2.62	3.33	+9
HO-CH ₂ -CH(CH ₃)-CH ₂ -CH ₂ -CH ₂ -OH + n-Octanoic Acid	0.916	15.40	8.88	6.55	2.71	3.51	—
 + n-Octanoic Acid	0.920	14.50	8.10	5.97	2.36	3.62	-35
Tetramethylene Glycol + i-Octanoic Acid	0.935	12.80	6.89	4.88	1.98	3.86	-72
2-Ethyl Hexanoic Acid + i-Octanoic Acid	0.929	15.50	8.68	5.18	2.37	3.75	-72
Methylhexamethylene Glycol + i-Octanoic Acid	0.915	18.20	9.20	6.50	2.48	5.70	-72
2-Ethyl Hexanoic Acid + i-Octanoic Acid	0.920	17.60	8.77	6.05	2.16	4.13	-72
2-Ethyl Hexanoic Acid + i-Octanoic Acid	0.950	22.00	11.80	8.2	2.94	3.64	-72
Leuna Carboxylic Acid Mixture (200/250)	0.936	23.53	12.20	8.60	3.20	5.44	-72
Leuna Carboxylic Acid Mixture (200/250)	0.932	29.60	14.80	9.97	3.40	3.63	-72
Leuna Carboxylic Acid Mixture (200/250)	0.950	32.90	15.40	10.00	3.21	3.90	-59

Table 5

Esters of Dicarboxylic Acids with Branched-Chain and Cyclic Alcohols as Compared with Straight-Chain Alcohols	Viscosity in cs., °C			m 20:99	Pour Point, °C
	38	50	99		
Adipic Acid + n-Octanol	8.75	—	2.85	3.09	-10
Adipic Acid + i-Octanol = 2-Ethyl-Hexanol	7.85	—	2.26	3.43	<-72
Adipic Acid + Cyclohexanol	27.70	12.90	4.42	(3.24)	-40
Adipic Acid + m- and p-Methylcyclohexanol	5.95	17.60	4.64	3.76	-52
Adipic Acid + i-Hexanol-2-Ethyl-Butanol	—	—	1.77	3.65	<-72
β-Methyladipic Acid+n-Octanol	9.22	6.67	2.90	3.16	-85
β-Methyladipic Acid+i-Octanol	—	—	2.61	3.65	<-72
β-Methyladipic Acid+cyclohexanol	—	—	—	3.95	-50
β-Methyladipic Acid+m- and p-Methylcyclohexanol	25.73	15.60	4.28	3.99	-46
β-Methyladipic Acid+i-Hexanol	—	4.77	2.02	3.72	<-72

Table 6

Esters of Dicarboxylic Acids	Spec. Gr. 20°C	Viscosity in cs., °C				m 20.99	Four Point, °C,
		20	38	50	99		
		Adipic Acid + n-Octanol	0.919	14.2	8.75		
Adipic Acid + n-Dodecanol	—	—	—	12.40	4.53	(3.05)	+56
α-Methyladipic Acid + n-Octanol	0.927	16.80	9.33	6.66	2.66	3.48	-32
α-Methyladipic Acid + n-Dodecanol	0.913	36.13	17.30	12.10	4.28	3.23	+16
β-Methyladipic Acid + n-Octanol	0.920	16.00	9.22	6.67	2.90	3.16	-36
β-Methyladipic Acid + n-Dodecanol	0.898	35.90	18.60	13.20	4.71	2.96	+10
Adipic Acid + Leuna Alcohol (100-250)	0.930	32.73	16.40	10.85	3.65	3.60	-69
α-Methyladipic Acid + Leuna Alcohol (100-250)	0.933	49.20	20.90	13.40	4.07	3.71	-60
β-Methyladipic Acid + Leuna Alcohol (100-250)	0.913	49.60	21.20	13.60	4.16	3.67	-59
Dimethyladipic Acid + Leuna Alcohol (100-250)	0.932	58.70	24.20	15.50	4.29	3.85	-57
Sebacic Acid + Leuna Alcohol (100-250)	0.916	44.10	20.70	13.90	4.45	3.48	-70
Adipic Acid + i-C ₉ Alcohols from "Oxo" Process on Diisobutylene	0.918	24.00	12.70	8.70	3.21	3.43	<-72
β-Methyladipic Acid + i-C ₉ Alcohols from "Oxo" Process on Diisobutylene	0.916	28.20	14.60	10.00	3.52	3.49	-70
Dimethyladipic Acid + i-C ₉ Alcohols from "Oxo" Process on Diisobutylene	0.916	30.73	15.00	10.41	3.59	3.39	-60
Sebacic Acid + i-C ₉ Alcohols from "Oxo" Process on Diisobutylene	0.911	38.35	19.50	13.40	4.71	3.20	-40

Table 7

Esters of Polyhydroxy Alcohols and Semiesters (HE) of Adipic Acid $\text{H}(\text{OC}-(\text{CH}_2)_4-\text{COOH})_2$ R-Leuna Alcohol 140/180	Spec. Gr. 20°C	Viscosity in cs., °C					m 20:99	Pour Point, °C
		20	38	50	99	20:99		
Ethylene Glycol + HE + n-C ₈ Acid	0.992 0.984	43.53 9.00	20.10 5.36	13.30 4.03	4.30 1.76	3.48 3.57	-62. +18	
Tetramethylene Glycol + HE + n-C ₈ Acid	0.993 0.919	57.70 11.77	26.80 6.85	17.20 5.17	5.38 2.29	3.35 3.38	-33 +13	
Hexamethylene Glycol + HE + n-C ₈ Acid	0.993 0.920	64.20 14.40	29.53 8.40	19.80 6.26	6.14 2.62	3.16 3.33	-19 + 8	
Methylhexamethylene Glycol + HE + n-C ₈ Acid	0.995 0.916	87.30 15.40	40.20 8.88	25.30 6.53	7.23 2.71	3.23 3.31	-60 -29	
Dimethylpropane + HE + n-C ₈ Acid	0.982 0.920	64.00 14.50	27.90 8.10	17.80 5.87	5.30 2.36	3.46 3.62		
Trimethylolthane + HE + n-C ₈ Acid	1.011 0.944	126 35.20	81.25 17.75	47.07 11.96	10.75 3.86	3.30 3.58	-51 - 8	
Pentaerythritol + HE + n-C ₈ Acid	1.021 0.959	482 50.79	177.7 23.80	101.1 15.69	19.50 4.73	3.04 3.50	-45 + 7	

Table 8

Increasing Molecular Size by Ethoxylation of the Alcohol Employed: 1-C ₉ Alcohol by "Oxo" Process on Diisobutylene		Spec. Gr. 20°C	Viscosity in cs., °C				Pour Point, °C	
			°C					
			20	38	50	99		
1-C ₉ Alcohol	+ 0 Mole C ₂ H ₅ O + Adipic Acid	0.918	24.00	12.70	8.70	3.21	3.43	-72
"	+ 1 " "	0.948	37.60	18.30	12.0	4.30	3.38	-65
"	+ 2 " "	0.976	59.00	27.40	18.50	5.74	3.26	-58
"	+ 4 " "	1.002	92.80	40.90	27.60	7.72	3.13	-52
"	+ 6 " "	1.021	124.60	54.10	34.80	10.00	2.97	-38
"	+ 0 " "	0.916	28.20	14.60	10.00	3.52	3.49	-70
"	+ 1 " "	0.950	46.00	21.90	14.70	4.73	3.40	-60
"	+ 2 " "	0.974	65.10	29.07	19.50	5.16	3.24	-55
"	+ 4 " "	0.996	98.00	42.30	27.10	8.31	3.06	-50
"	+ 6 " "	1.038	180.00	75.20	47.01	12.50	2.92	-16
Leuna Alcohol 180/250	+ 2 " Adipic Acid	0.972	53.90	24.60	15.70	4.86	3.46	-59
"	+ " " Methyladipic Acid	0.980	78.50	32.80	21.40	6.25	3.38	-54
"	+ " " Sebacic Acid	0.969	119.20	50.60	31.30	8.96	3.10	-55

Figure 9 - - EXPERIMENTS ON

THE CHAIN MACHINE.

- 1 - Adipic Acid + n-Butanol 1.23
- 2 = " " + n-Octanol 1.51
- 3 = " " + n-Dodecanol 2.06
- 4 = β -Methyladipic Acid + n-Octanol 1.55
- 5 = β - " " + n-Dodecanol 2.07

E 60

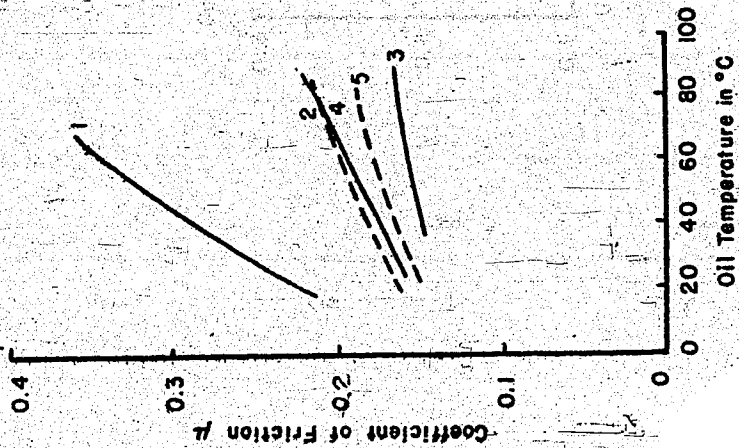
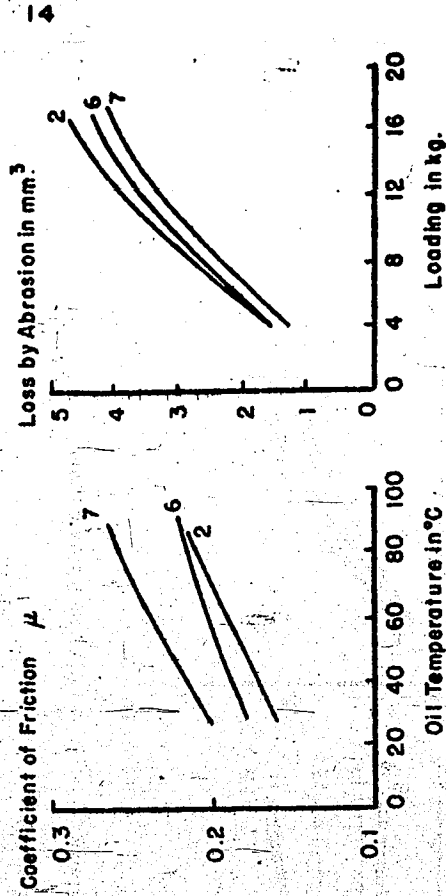


Figure 10 - EXPERIMENTS ON

THE CHAIN MACHINE.

- 2 - Adipic Acid + n-C₈-Alcohol (350)
 - 6 = " " + i-C₈ "
 - 7 = Methyladipic Acid + i-C₈-Alcohol (363)
- Hard Metc. Disk against Steel;
Length of Experiment, 10 min.;
Oil Temperature, 20 °C



WEAR EXPERIMENTS

EXPERIMENTS ON THE CHAIN MACHINE.

25 = Trimethylolethane + Leuna
Carboxylic Acid
11 = Trimethylolethane + *i*-C₆
Acid.

12 = Trimethylolethane + Tap Cut
Fatty Acid C₇-C₉
13 = Trimethylolethane + 3 Mol *i*-
C₁₃-Acid
17 = " " + 2 "
16 = Pentaerythritol + 4 "

Hard Metal Disk against Steel;
Length of Experiment, 10 Min.;
Oil Temperature, 20°C.

Hard Metal Disk against Steel;
Length of Experiment, 10 Min.;
Oil Temperature, 20°C.

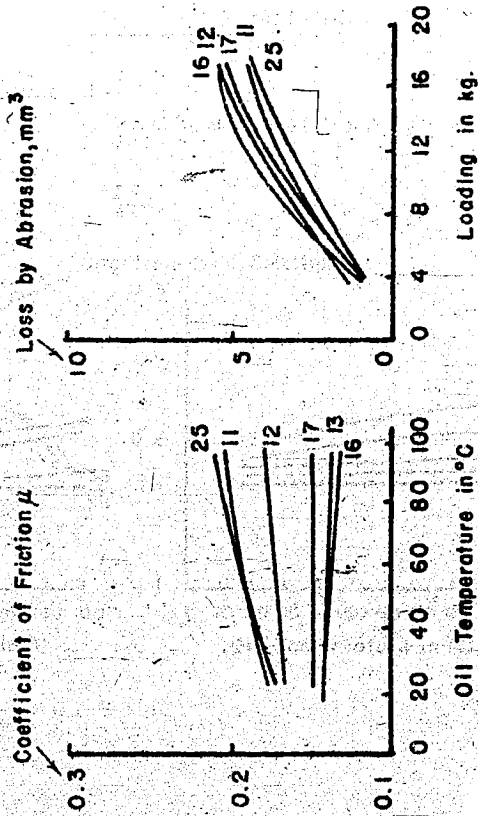


Figure 12.

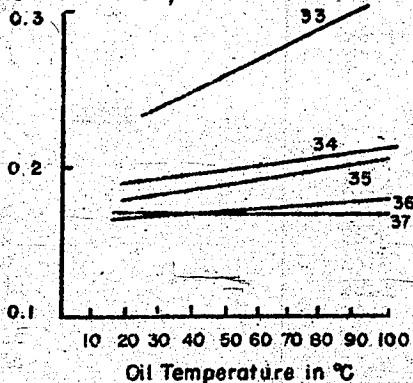
EXPERIMENTS ON THE CHAIN MACHINE.

$iC_4-(OCH_2-CH_2)_x$ + MethyladipicAcid

- 33: X = 0
- 34: X = 1
- 35: X = 2
- 36: X = 4
- 37: X = 6

- 42 = iC_9 Alcohol + 0 Mol C_2H_4O + AdipicAcid
- 43: " + 1 " " "
- 44 " + 2 " " "
- 45 " + 4 " " "
- 46 " + 6 " " "

Coefficient of Friction μ .



Coefficient of Friction μ .

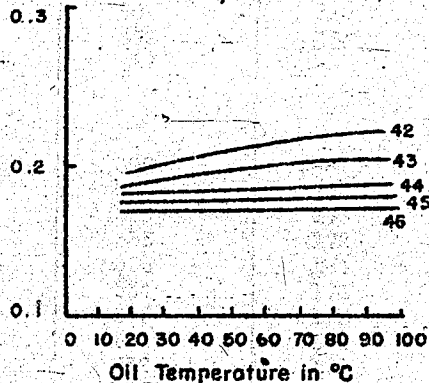


Table 13 Energies of Adhesion for Various Substances
against Mercury (at 20°C) according to Measurements of
K. L. Wolff and Coworkers, Halle

Substance	Surface Tension (dynes/cm.)	Interfacial Tension (dynes/cm.)	Energy of Adhesion (ergs/cm. ²)
<u>Hydrocarbons</u>			
Hexane	19.5	---	120
Cyclohexane	24.7	377	120
Benzene	28.6	366	---
<u>Alcohols</u>			
Methanol	22.5	384	119
Ethanol	22.4	---	---
n-Propanol	23.7	373	125
i-Propanol	23.7	384	117
n-Butanol	24.8	377	---
i-Butanol	---	384	116
n-Hexanol	26.4	372	154
n-Octanol	27	367	---
<u>Acids</u>			
Formic	37.4	393	---
Acetic	27.4	334	174
Propionic	26.5	333	174
n-Butyric	26.6	335	172
n-Valeric	27.4	355	174
n-Hexanoic	28.1	334	174
n-Heptanoic	28.3	335	173
n-Octanoic	28.7	334	175
n-Hexanoic	29.9	332	170
<u>Esters</u>			
Methylacetate	24.9	---	117
Ethyl-	25.0	---	120
n-Propyl-	24.3	---	124
i-Propyl	23.1	369	134
n-Butyl	24.5	374	131
sec-Butyl	23.5	354	150
i-Butyl	22.8	355	140
n-Amyl	25.5	365	141
i-Amyl	24.8	345	---
n-Hexyl	26.3	365	141
n-Heptyl	27.1	357	150
n-Decyl	28.7	343	166
n-Dodecyl	29.1	341	160

Table 14 Differences in Energy of Adhesion against Aqueous and Metallic Surfaces according to Measurements of K. L. Wolff, Halle

Substance	Interfacial Tension (dynes/cm.) against		Energy of Adhesion H (ergs/cm. ²) against	
	Water	Mercury	Water	Mercury
Hexane	51.25	380	40.0	120
Benzene	55.05	366	56.6	143
CCl ₄	43.26	358	56.1	149
C ₆ H ₅ Cl	37.41	350	58.5	163
CS ₂	48.36	341	55.8	170
Mercaptan	25.12	340	68.5	160
Octanol	8.52	367	90.8	140
Heptanoic Acid	6.96	335	94.6	173
Ester	ca. 25	ca. 350	ca. 75	ca. 150

Table 15 Rupture Resistance and Adhesive Resistance
according to Calculations of Prof. Wolff at Halle

Substance	Rupture Resistance (kg./cm. ²)	Adhesive Resistance (kg./cm. ²)
Cyclohexane	4900	12500
Benzene	5600	14300
CCl ₄	5500	15000
Ethanol	4500	12000
Propanol	4700	12500
Butanol	5000	12800
Hexanol	5300	13400
Propionic Acid	5300	17400
Butyric Acid	5300	17200
Hexanoic Acid	5500	17400
Heptanoic Acid	5700	17400
Water	14400	16700
Mercury	96000	96000
Brass	5000	
Iron	4000-7000	

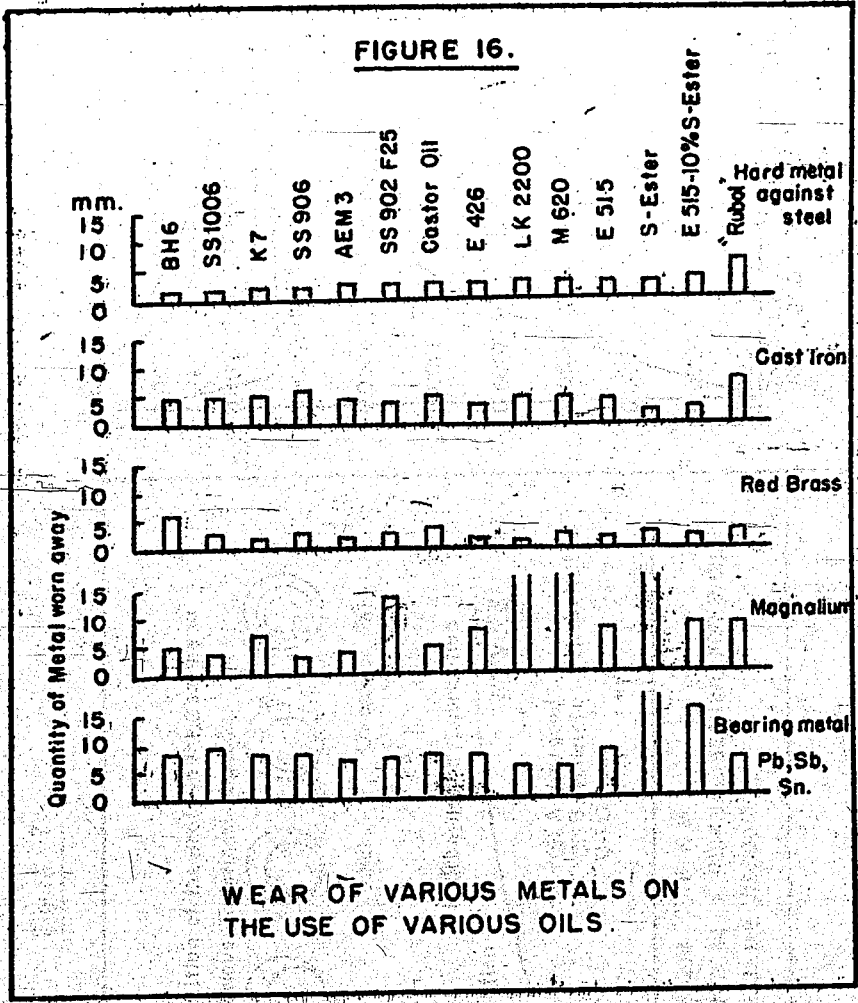
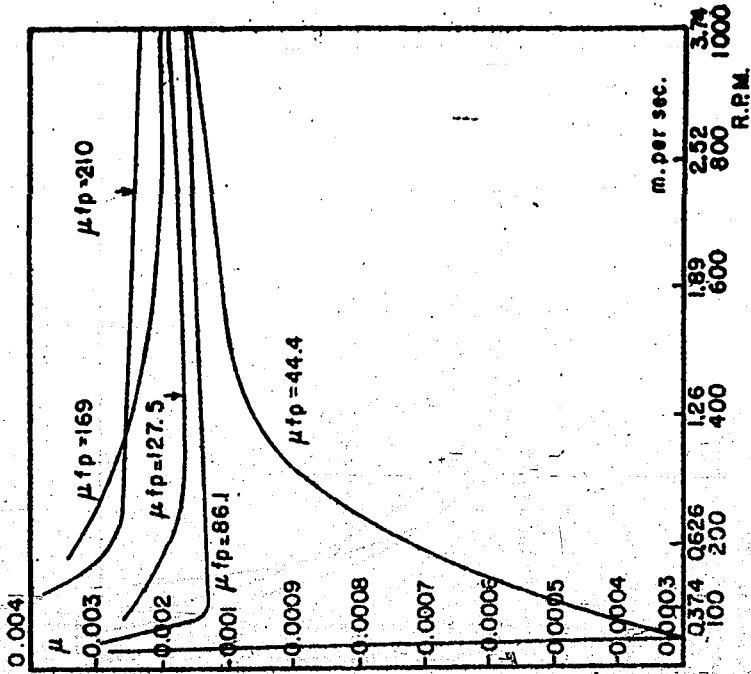


Figure 18



Babbitt Metal: 74 Pb. 14.9 Sb. 6.9 Sn. 2.0 Cd. 1.0 Cu. 1.3 Ni
 Clearance 0.25 mm. Oil Pressure 3.5 at. Oil Temperature 30°C. Oil B.C.B. Coefficient of Friction μ - Temp. in Oil Film.

Figure 17

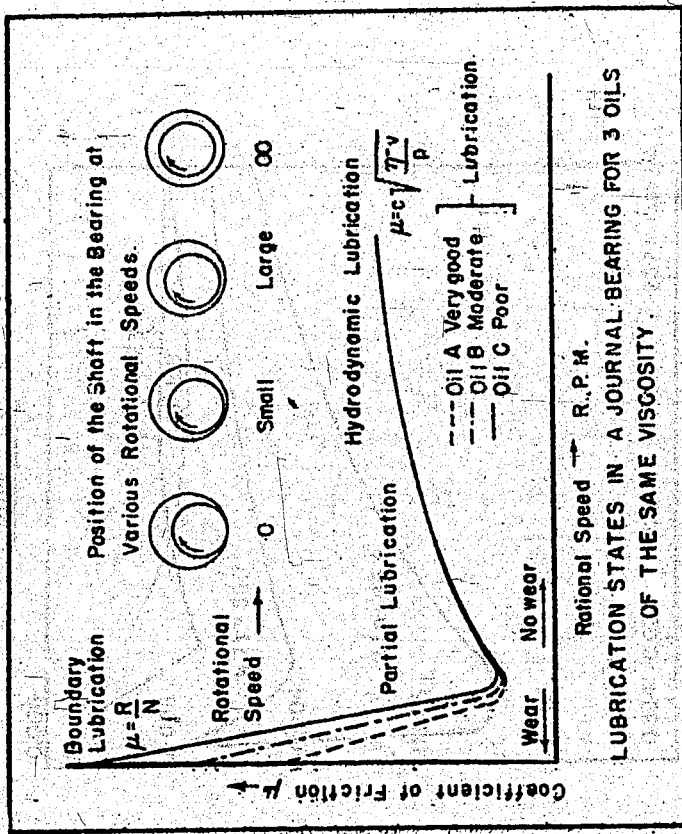
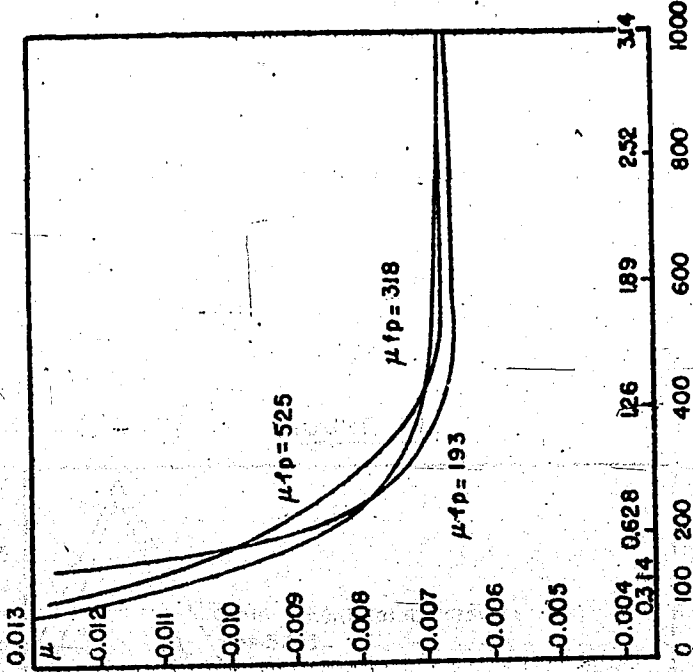


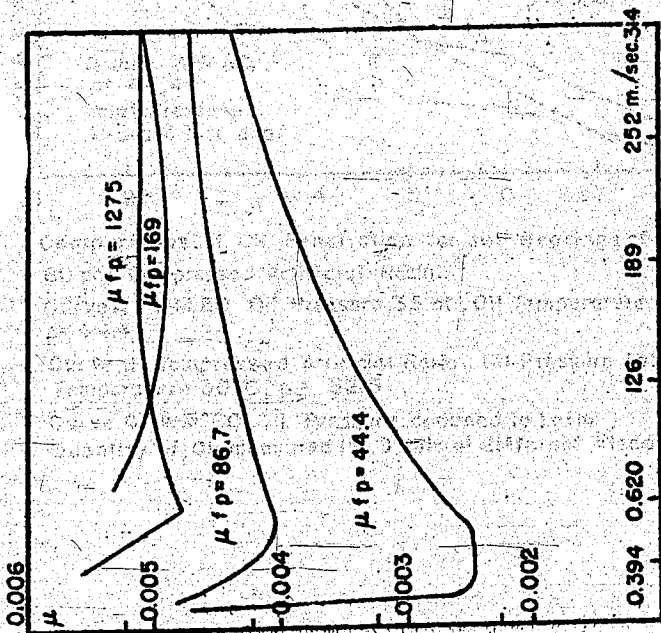
Figure 20.



Bearing of Compressed Artificial Resin Type T₂ Cloth Packing,
Oil BC8, Oil Pressure 1atm., Oil Temperature 30°C, Clearance
0.25 mm.

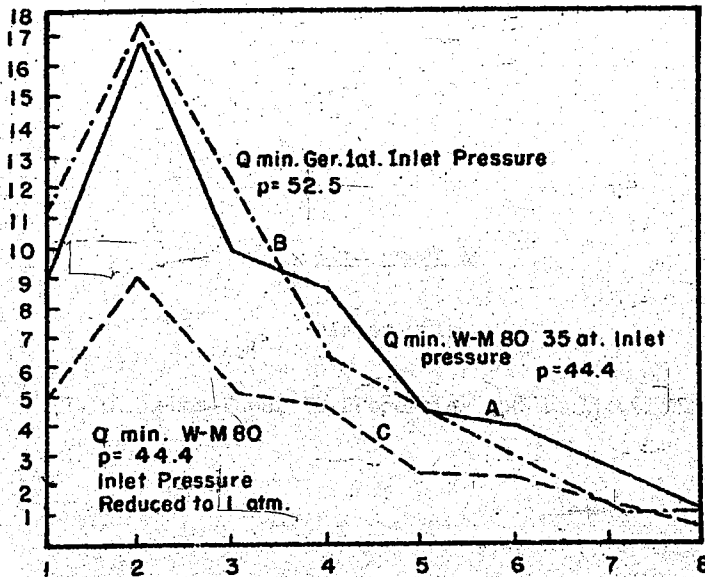
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Figure 19.



Babbitt Metal : 81.63 Pb, 14.5b, 0.5Sn, 3.07 As, 0.98 Cu,
0.01 Ni. Clearance, 0.25 mm. Oil Pressure, 3.5 at. Oil Temperature,
30°C. Oil BC 8.

FIGURE 21



Comparisons of Oil Penetration for two Bearings of W-M 80 and Compressed Artificial Resin.

Curve A: WM 80 Oil Pressure 35 at., Oil Temperature 30°C, $p = 44.4$.

Curve B: Compressed Artificial Resin. Oil Pressure 1 at., Oil Temperature 30°C, $p = 52.5$

Curve C: WM 80, Oil Pressure reduced to 1 atm.

Quantity of Oil measured for 8 Oils of different Viscosity.